

AGING CHARACTERISTICS OF COAL LIQUIDS

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INTRODUCTION

Materials handling and storage is an important part of any chemical process. The SYNTHOIL process (1), which converts coal to a low-ash, low-sulfur fuel oil, requires careful storage to control the viscosity of the product. The economics of this process requires a light hydrogenation of coal, and therefore any chemical changes during storage that may increase the viscosity of the product to a level at which it becomes a handling problem must be avoided. Recommended handling procedures can be determined by laboratory studies. Previous studies (2,3) give a brief resume of the changes in viscosity of SYNTHOIL samples during ambient storage for times up to 120 days. The present report, also based on viscosity measurements, covers a variety of storage conditions which include storage temperatures of 30°-61°C, atmospheres of nitrogen, air and oxygen, both stirred and unstirred samples and ambient light versus darkness. Further studies of these samples based on chemical and instrumental analyses will be reported.

EXPERIMENTAL

Aging tests were made on three coal liquids from SYNTHOIL run FB-53. Run FB-53 was made with a West Virginia coal, (Pittsburgh Seam, hvAb) and operated at 4000 psig H₂ and 450°C. Pelleted CoO-MoO₃-SiO₂-Al₂O₃ catalyst was used in the reactor. The samples investigated were from Batches 1, 21, and 50 which were obtained after 4, 84, and 200 hours, respectively, of operation of the coal liquefaction reactor.

The most comprehensive aging tests were made on the Batch 1 sample. After an initial viscosity measurement, a 200 ml sample of this batch was transferred to each of fifteen one-liter containers. Each sample was simultaneously connected to the aging apparatus and there subjected to a particular combination of the aging factors. Periodically ~10 g samples were removed from the aging containers and viscosity measurements made. All viscosity measurements were made with a Brookfield viscometer which permitted measurements at various temperatures. Thus, viscosity measurements were made at two temperatures, 30°C and 61°C, by circulating water from the aging baths through the heating jacket of the viscometer.

Similar, though less extensive, aging tests were performed on samples from Batches 21 and 50 from run FB-53. Data accumulation was limited because of the high initial viscosities of these samples and their rapid rate of change.

RESULTS AND DISCUSSION

The results of the aging tests are presented in Figures 1-3. The graphs represent the change in viscosity that occurs with aging time; infrared spectra in the figures were obtained on thin films of representative samples.

Figure 1 shows the changes in viscosity that occur when Batch 1 samples are stored at 61°C, stirred, exposed to light and subjected to one of the three

test gases, oxygen, air or nitrogen. In this and all subsequent figures, exposure to oxygen had the most pronounced impact upon the increase in viscosity; exposure to air had the next strongest impact. A small change was noted for the samples exposed to nitrogen. Also included in Figure 1 are the results for Batch 50 samples aged at the same conditions, i.e., 61°C, exposed to light and exposed to oxygen, air or nitrogen. As the figure shows, the initial viscosity of these samples is much greater than that for Batch 1 which was obtained early in the run. The much more rapid increase in viscosity of these Batch 50 samples confirms previous work (2).

The most significant viscosity increases occurred in samples exposed to oxygen. Hydrocarbon oxidation is confirmed by the infrared spectra shown in Figure 2. The spectrum obtained from the fresh reactor oil and spectra from oils exposed to different gases differ at 1690 cm^{-1} which has been assigned to carbonyls that have been formed during aging. That the formation of this band is progressive (continues throughout the aging process) can be shown by the gradual increase of the carbonyl absorption. There are many ways in which this light oxidation of SYNTHOIL may cause the observed viscosity increase. The formation of carbonyls represents a small increase in molecular weight. Carbonyls might combine with phenols as hydrogen bonded molecules or as polymers, or oxidation may proceed by way of peroxide formation and a free-radical mechanism. The ultimate objective of this work is the identification of an appropriate mechanism and the development of an inhibitor. Lin (4) has made some helpful observations.

The observed increase in viscosity for a sample stored under nitrogen may be explained in several ways. There may be a physical agglomeration similar to the crystallization of a solid from a supernatant liquid. There may be a chemical interaction between the acidic and basic components which are known to be present in SYNTHOIL (5). Further, there may be a volatilization of the lighter components under the influence of heat and stirring. Volatility effects were minimized by using a slow gas input and covered containers.

Figure 3 shows the results for samples exposed to the same gases, but aged at 45°C. The same ordering of increased viscosity of samples relative to the exposure gas as noted for the samples stored at 61°C is found; i.e., oxygen > air > nitrogen. Figure 3 also contains data for Batch 21 stored at 45°C. As noted previously, these results show that faster rates of increase in viscosity occur for samples with higher initial viscosities.

Viscosity data were obtained at 30°C for the nine samples aged in the three gases and at three temperatures. Similar relationships to those found for the viscosity measurements at 61°C are apparent. One distinction is that the changes noted for the samples exposed to nitrogen and air appear more severe. This is undoubtedly due to the substantially higher initial viscosity occasioned by the lowering of the temperature at which the viscosities were measured. An examination of the melting points of typical benzenoid molecules makes it apparent that there will be wide variations of viscosity with temperature.

The effects of not stirring the sample and not exposing the samples to ambient light were observed. A significant reduction in the aging of the samples exposed to either oxygen or air occurs when the particular sample is not stirred; the sample exposed to nitrogen shows no change. This obviously indicates that stirring merely exposes new sample constantly to the oxygen in the gaseous environment; i.e., there is no intrinsic effect due to mechanical agitation of

the sample. In addition, these results also indicate that the ambient light of the laboratory has essentially no impact on the aging properties of these samples. Further study of sunlight or other UV sources would be necessary.

Solvent separations made using the original sample, a sample after 35 days storage at 61°C under nitrogen, and a sample after 28 days storage at 61°C under oxygen gave the following data:

	Oil	Yield, Percent by Weight		Ash
		Asphaltene	Benzene Insol.	
Original	73	20	7	3
N ₂ Storage	75	18	7	3
O ₂ Storage	62	20	18	3

For this table Oil is defined as benzene soluble, pentane soluble materials and Asphaltene as benzene soluble, pentane insoluble materials. As the data indicate, no changes in component distribution occurred for the sample stored under N₂, while the sample stored under O₂ showed a decrease in oil and a corresponding increase in benzene insoluble materials. This increase in benzene insoluble material may indicate polymer formation.

CONCLUSION

These data provide some insight into the effects of time, heat, light, mechanical agitation, and gaseous environment on SYNTHOIL aging. Further analyses underway include solvent and chromatographic separations and spectral identification of the aging products. These should help to establish a mechanism for aging and perhaps suggest inhibitors which will improve the storage characteristics of SYNTHOIL.

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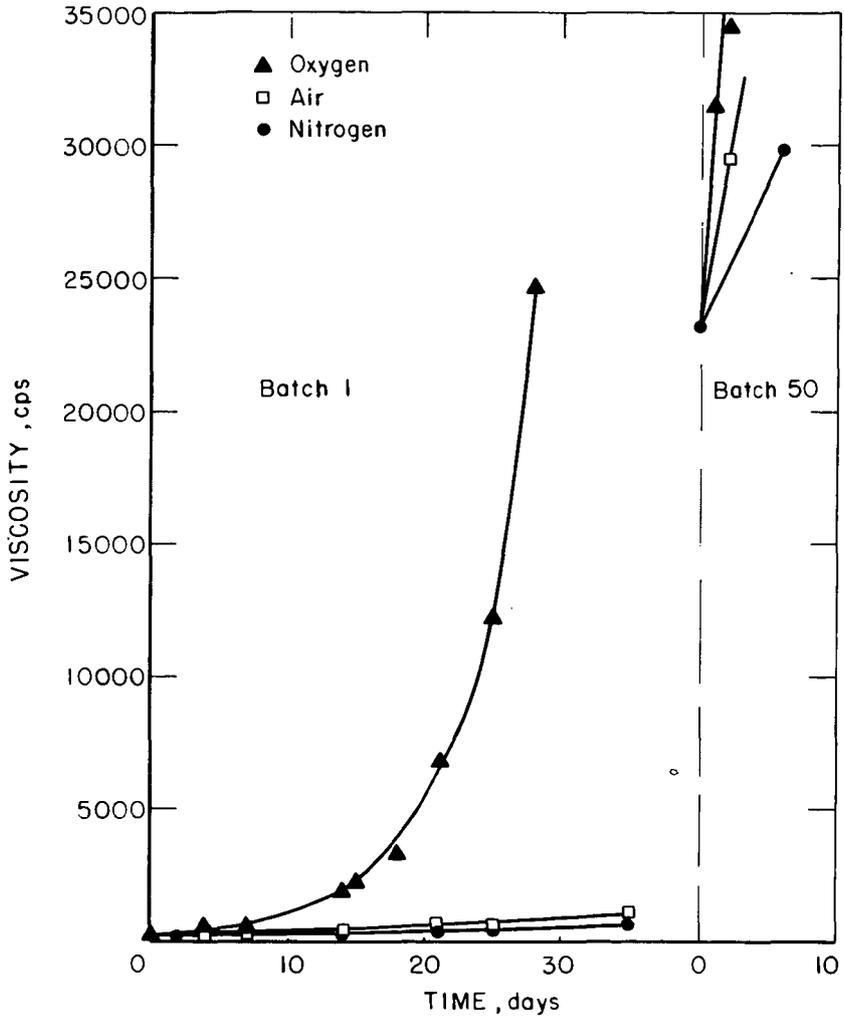


Figure 1 -Viscosity change with storage time Storage at 61°C, viscosity at 61°C .

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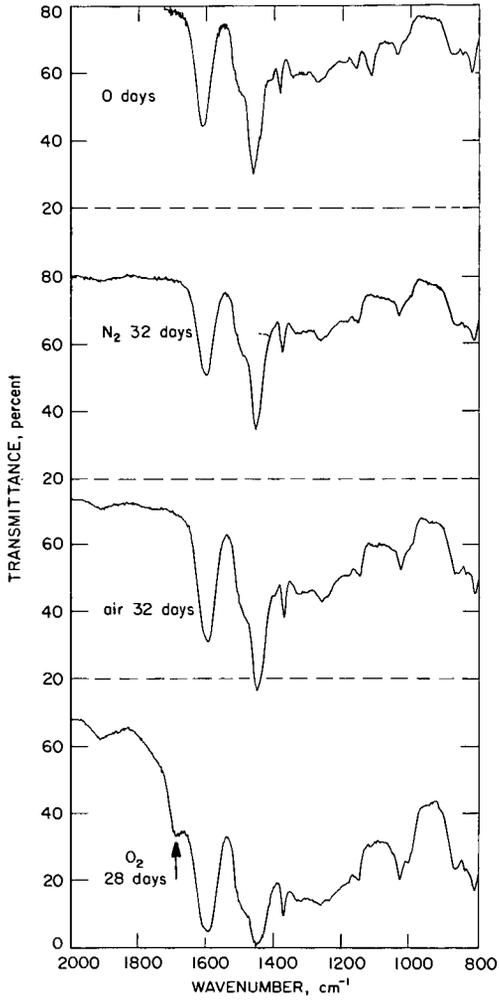


Figure 2 - Infrared spectra showing the increase of C=O during SYNTHOIL storage in various gases.

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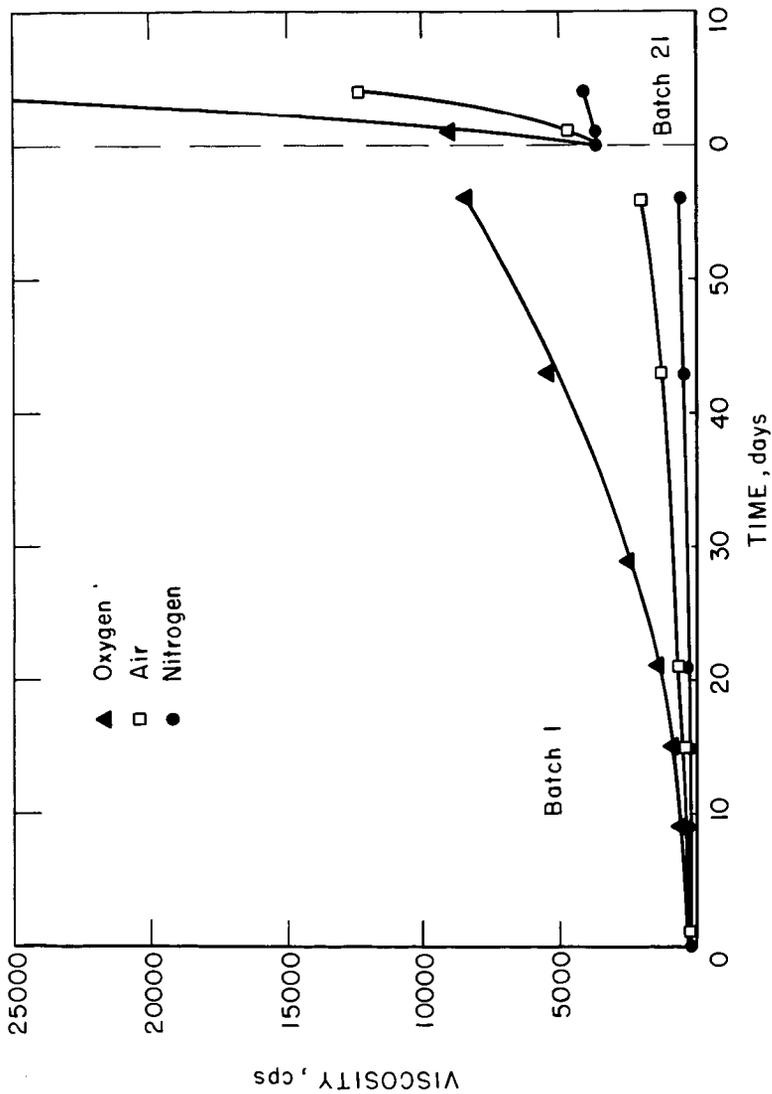


Figure 3 - Viscosity change with storage time Storage at 45°C, viscosity at 61°C

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